Photochemical Regulation of Stratospheric Ozone: Constraints from \cdot Recent Aircraft, Balloon, and Satellite Observations

Ross J. Salawitch, ASHOE/MAESA Science Team, ATMOS/ATLAS- 3 Science Team, SAO/FIRS Sciene Team, JPL/BMLS Science Team

Corresponding address: Ross Salawitch, JPL, M.S. 183-301,
4800 Oak Grove Dr., Pasadena, CA 91109
rjs@caesar.jpl.nasa.gov

A photochemical model constrained by observed concentrations of long lived radical precursors, aerosol surface area, and environmental factors (i.e., ozone column, albedo, profiles of aerosol extinction) is used to examine our understanding of the height, latitude, seasonal, and aerosol surface area dependence of the concentration of hydrogen, nitrogen, chlorine, and bromine radicals, the photochemical loss rate of ozone, and the balance between photochemical production and 1 oss of ozone (McElroy et al. , 1992; Salawitch et al. , 1994a,b; Wennberg et al., 1994). The model provides a framework for interpreting measurements of dozens of gases and related quantities (i .e.aerosol surface area and albedo) obtained during recent ER- 2 expeditions (AASE, AASE 11, SPADE, and ASHOE/MAESA), balloon deployments of the FIRS (Far Infrared Spectrometer) and BMLS (Balloon Microwave Limb Sounder) instruments, and recent observations obtained by ATMOS (Atmospheric Trace Molecule Spectroscopy Experiment) and SAGE 11 (Stratospheric Aerosols and Gas Experiment) .

Our analysis of measurements obtained during SPADE revealed more efficient catalytic removal of ozone by hydrogen and halogen radicals than predicted by models using recommended rates and cross sections (Salawitch et al., 1994a; Wennberg et al., 1994) and discrepancies in our understanding of the partitioning of NO and NO2 and of HCl anti other inorganic chlorine species (Jaegle et al., 1994; Webster et al., 1994). Models allowing for revised values of the quantum yield of O(1D) from photolysis of 03, temperature dependent absorption cross sections for HNO3, and heterogeneous decomposition of HNO4 to form HNO2 were shown to provide an excellent description of the observed variation of hydrogen, nitrogen, and chlorine radicals with solar illumination, although discrepancies persist between theoretical and observed HCl (Salawitch et- al., 1994b). The rapid heterogeneous hydrolysis of BrNO3 provides sufficient build-up of HOBr to also account for the anomalous rise of OH and HO2 observed during sunrise.

Our talk will focus on recent advances in our understanding of the partitioning of radicals and reservoir species of t_he hydrogen, nitrogen, and chlorine family gained from observat.ions obtained during the ASHOE/MAESA field campaign and the recent flight of ATMOS. In addition, we will comment on observations of ClO, HOCl, ClONO2, OH, HO2, NO2, and O3 obtained from ATMOS and a simultaneous deployment of FIRS and BMLS that demonstrate production and loss rates of ozone nearly balance at an altitude of 38 km, reconciling a long standing discrepancy in stratospheric chemistry (Jucks et al., submitted, 1995).

References

Jaegle, L. et al., In situ measurements of the NO2/NO ratio for testing atmospheric models, Geophys. Res. Lett., 21, 2555-2558, 1994.

McElroy, M. B., R. J. Salawitch, and K. Minschwaner, The changing stratosphere, Planet. Space Sci., 40, 373-401, 1992.

Salawitch, R. J. et al., The distribution of hydrogen, nitrogen, and chlorine radicals in the lower stratosphere: imp] i cations for changes in 03 due to emission of NOy from supersonic aircraft, Geophys. Res. Lett., 21, 2547-2550, 1994a.

Salawitch, R. J. et al., The diurnal variation of hydrogen, nitrogen, and chlorine radicals: implications for the heterogeneous production of HNO2, Geophys. Res. Lett., 21, 2551-2554, 1994b.

Webster, **c.** R. et al., Hydrochloric acid and the chlorine budget of the stratosphere, Geophys. Res. Lett., 21, 2575-2578, 1994.

Wennberg, P. O. et al., Removal of stratospheric ozone by radicals: in situ measurements of OH, HO2, NO, NO2, ClO, and BrO, Science, 266, 398-404, 1994.